

**ELECTRO-OPTICS BASED ON NOVEL MATERIALS
MODIFICATIONS**

Final Progress Report

**R. G. Wilson
R. N. Schwartz**

Contract No. DAAH04-95-C-0043

June 1998

U.S. Army Research Office

DAAH04-95-C-0043

19981222 136

HRL Laboratories, LLC

Approved for Public Release; Distribution Unlimited

The views, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

DTIC QUALITY INSPECTED 3

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	24 Jun 98	Final Progress 1 Jun 95 - 31 May 98	
4. TITLE AND SUBTITLE Electro-Optics Based on Novel Materials Modifications			5. FUNDING NUMBERS DAAH04-95-C-0043
6. AUTHOR(S) Dr. R. G. Wilson Dr. R. N. Schwartz			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) HRL Laboratories, LLC 3011 Malibu Canyon Road Malibu, CA 90265			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING/MONITORING AGENCY REPORT NUMBER ARO 32724.1-EL
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (maximum 200 words) Aims or goals of this work included growth, doping and characterization of new materials of interest to ARO for electro-optics and electronics applications within the DoD, often involving support for university research through collaborative programs initiated by Dr. John Zavada. A concomitant goal was the publication of papers that describe the results of this work and these collaborations. Results and significance of this work are described in the publications listed at the end of this report. Included are: successful growth of Er-doped (grown and implanted) nitrides and 1.54-mm stimulated light emission; characterization of p-and n-type commercial SiC; characterization of SiGeC and GeC films and oxidized AlN films for ARO applications; and measurement of the stability and of H (and its diffusion) in ScAlMgO ₄ , SiC, LiAlO ₂ , and LiGaO ₂ , all substrate for III-nitrides growth, especially GaN; stability of hydrogen in 6H and 3C SiC; work with SiGeC and GeC; characterization of III-nitrides grown in a variety of laboratories; and stimulated emission of 1.5-mm light from Er doping of all such materials, for optical communications systems applications; band edge luminescence measurements; and PL measurements.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Electro-Optics Based on Novel Materials Modifications

ARO Contract Number DAAH04-95-C-0043

Period covered: 1 June 1995 through 31 May 1998

Performed at: Hughes Research Laboratories

Principal Investigators: Drs. R.G. Wilson and R.N. Schwartz

Introduction and purpose for this program

This report describes work done and results obtained from 1 June 1995 through 31 May 1998. The report is divided into sections by technical area.

Aims or goals of this work included growth, doping, and characterization of new materials of interest to ARO for electro-optics and electronics applications within the DoD, often involving support for university research through collaborative programs initiated by Dr. John Zavada. A concomitant goal was the publication of papers that describe the results of this work and these collaborations.

The principal investigators for this program were Drs. R.G. Wilson and R.N. Schwartz of Hughes Research Laboratories. This report was prepared by R.G. Wilson.

Summary of Results

Results and significance of this work are described in the publications listed at the end of this report. Included are: successful growth of Er-doped (grown and implanted) nitrides and 1.54-mm stimulated light emission; characterization of p- and n-type commercial SiC; characterization of SiGeC and GeC films and oxidized AlN films for ARO applications; and measurement of the stability and of H (and its diffusion) in ScAlMgO₄, SiC, LiAlO₂, and LiGaO₂.

all substrates for III-nitrides growth, especially GaN; stability of hydrogen in 6H and 3C SiC; work with SiGeC and GeC; characterization of III-nitrides grown in a variety of laboratories; and stimulated emission of 1.5-mm light from Er doping of all such materials, for optical communications systems applications; band edge luminescence measurements; and PL measurements.

p- and n-type commercial SiC

The availability of good commercial p- and n-type SiC material is important for device fabrication. We characterized, using SIMS, such material grown by CREE and supplied by Lisa Porter of Prof. R.F. Davis' group at NCSU. Depth profiles of Al-doped p-type SiC and of N-doped n-type SiC both grown on the opposite type of SiC were measured. The Al density decreased from about $1 \times 10^{18} \text{ cm}^{-3}$ at the surface to about $3 \times 10^{17} \text{ cm}^{-3}$ at the interface, through a 5- μm thick film. The N was apparently grown in two layers with slightly different doping densities of about 3 and $4 \times 10^{19} \text{ cm}^{-3}$.

p- and n-type commercial GaN

The availability of good commercial p- and n-doped GaN material is important for device fabrication. We characterized, using SIMS, such material grown by EMCORE and supplied by Prof. S. J. Pearton of the Univ. of Florida. Depth profiles of Mg-doped p-type GaN and of Si-doped n-type GaN both grown on sapphire were measured. The Si was quite uniform at about $2.5 \times 10^{18} \text{ cm}^{-3}$ in a 3.6- μm thick layer, as shown in Fig. 1. The Mg was less uniform at between 1 and $5 \times 10^{19} \text{ cm}^{-3}$ in a 0.8- μm thick layer, as seen in Fig. 2. There was also a substantial pile-up of Mg at the substrate interface.

H in various materials

The redistribution or diffusion of H in selected materials was studied by implanting H into the near surface of those materials, or treating the surface of those materials with a hydrogen plasma. ^2H is often used because of the enhanced detection of ^2H compared with ^1H when secondary ion mass spectrometry (SIMS) is used to determine the depth profile or distribution of the hydrogen.

The materials studied for hydrogen redistribution included sapphire, SiC, LiAlO₂, LiGaO₂, and ScAlMgO₄, all substrates used for MOCVD or MBE growth of epitaxial layers of III-nitrides (e.g., GaN and AlN), Ge (bulk and epitaxially grown on Si) and GeSi epitaxialloy grown on Si, and bulk Si. This work involved collaboration with Prof. S. J. Pearton of the University of Florida, Fan Ren of Lucent Technologies Bell Laboratories, and Prof. James Kolodzey of Univ. Delaware. LiAlO₂ and LaGaO₂ were supplied by Bruce Chai of University of Central Florida; ScAlMgO₄, by Pearton; the SiGe/Si, by Kolodzey, and the Ge by Wilson of HRL.

This work was quite successful and resulted in a number of papers, in which the details of the experimental work and the results of the work are described. See publications 1, 3, 4, 6, 7, 8, 11, 14, 17, 20, 29, 32, 36, 37, 38, and 41. Conclusions include: 1) H is thermally stable in SiC, no redistribution or diffusing occurring until a temperature greater than 1125°C is reached. 2) H is thermally stable in LiAlO₂ and LiGaO₂ up to temperatures at which they roughen or begin to decompose, temperatures below which good III-nitrides are best grown using MOCVD or MBE. Thus these two materials are no longer being considered as substrates for III-nitride growth. H is stable in ScAlMgO₄ up to a temperature near 600°C; in Ge, at temperatures up to about 250°C; and in SiGe, at temperatures up to about 450°C.

The preparation of implanted SIMS quantification standards in these various materials was a significant part of this work.

Hydrogen in SiC and diamond

²H was implanted (100 keV and 2.0x10¹⁵ cm⁻²) into a moderately large piece of SiC grown by CREE and supplied to us by Prof. R.F. Davis of NCSU. This piece was subsequently broken into smaller pieces, which were annealed at temperatures of 400, 500, 600, 700, 800, 875, and 950°C for 10 min in flowing dry nitrogen. The unannealed and annealed pieces were then depth profiled using SIMS. No redistribution of ²H was observed in any of these samples. H had been observed to redistribute in Si beginning at temperatures less than 300°C, for reference. Pieces of this implanted SiC were subsequently annealed at temperatures of 1000, 1050, 1100, 1150, and 1200°C. The H finally began to diffuse toward the surface (through the damaged region) at 1150°C, in the same manner as was measured for Si, but at much lower temperatures. The H did not diffuse into the undamaged bulk of the SiC even at 1200 °C. The results of this

work are reported in references 14 and 15. Figure 3 shows the key results of this work.

^2H was also introduced into samples of the same SiC material by treatment in a deuterium plasma at University of Florida (S.J. Pearton). These samples were SIMSed at the same time and under the same conditions as the previously described implanted samples. The results are described in reference 15. More samples of SiC were treated with an ECR ^2H plasma and subsequently annealed (by Pearton). These samples were then SIMSed; some results are shown in Fig. 4.

A diamond crystal was implanted with ^2H and the resulting depth distribution was measured using SIMS. The profile is shown in Fig. 5. From previous work we know that H does not redistribute in diamond for temperatures up to 1000°C. Above this temperature, the atmosphere in which diamond is thermally treated must be carefully controlled because the presence of any oxygen will cause the diamond to burn.

Hydrogen in other substrate materials used for III-nitride growth

Materials that are used as substrates for III-nitride growth include SiC, sapphire, the newer, more nearly lattice matched LiAlO₂ and LiGaO₂, and potentially ZnO and ScAlMgO₄. A study of H diffusion in SiC was described above. We carried out similar studies for sapphire, LiAlO₂, LiGaO₂, and ScAlMgO₄. Samples of these materials were implanted with ^2H , annealed at 300, 400, 500, 600, 700, 800, and/or 900°C, and SIMSed. Some of the results are shown in Fig. 6 for sapphire, in Fig. 7 for LiAlO₂, in Fig. 8 for LiGaO₂, and in Fig. 9 for ScAlMgO₄. No redistribution of H in sapphire was observed. For LiAlO₂ and LiGaO₂, redistribution of H is seen to begin around 400°C, with H loss from the crystal progressing with increasing temperature up to 800°C when it drops below the detection limit of the SIMS measurement (about 10^{15} cm^{-3}). This work was published in Applied Physics Letters at the end of 1996; see publication 20. The data for ScAlMgO₄ are reported in references 24 and 41. Hydrogen is seen (Fig. 9) to redistribute at temperatures of 500°C and higher.

For ScAlMgO₄, redistribution begins at about 500°C - the peak of the depth profile shifts slightly toward the surface as if into the damage depth distribution. Then it drops sharply in density to 700°C, apparently without first piling up near the surface -- it just leaves the material through the surface and apparently into the material. It is entirely gone at 800 and at 900°C, leaving no residual level in the material above 10^{17} cm^{-3} .

LiAlO_2 and LiGaO_2 were also treated in a ^2H plasma and some of that material was also annealed at 500°C . The resulting depth distributions measured using SIMS are shown in Fig. 10, panes a and b, respectively. H is seen to penetrate LiAlO_2 more readily than LiGaO_2 .

For a ^2H plasma-treated sample of ScAlMgO_4 , the ^2H barely penetrates the ScAlMgO_4 ; its density is high at the surface ($\sim 10^{21} \text{ cm}^{-3}$) but drops to what looks like a 10^{17} cm^{-3} detection limit in the first 15 nm, as shown in Fig. 11.

Er-doped III-nitrides

Prof. C. Abernathy at the University of Florida grew Er-doped GaN for study in 1996, following the successful growth of Er-doped AlN during 1995. See references 9. GaN films doped with about $3 \times 10^{18} \text{ cm}^{-3}$ Er were grown on sapphire.

A multilayered structure for an Er-doped device was grown near the end of this program. The surface layer was a Mg-doped p-layer, followed by an Er-doped layer, beneath which was grown a Si-doped n-layer. This structure was depth profiled using SIMS for the Mg, Er, and Si dopants, and C and O impurities. The results are shown in Fig. 12. An Er doping density of about $2 \times 10^{20} \text{ cm}^{-2}$ was achieved. An even higher density of Mg was obtained at the surface. The densities of C and O are somewhat high but they may enhance the emission of $1.54\text{-}\mu\text{m}$ radiation from the Er-doped region. Information about a device fabricated from this structure may be given in a future ARO-sponsored program.

We implanted Er into four samples of GaN from four laboratories, UCSB, HRL, EMCORE, and Carnegie Mellon Univ., annealed them at 650°C , and sent them to Prof. H Jiang at Kansas State Univ. for bandedge luminescence measurements, who then sent them to Prof. Uwe Hoemmerich at Hampton Univ. for 1.54-mm PL measurements. We subsequently re-annealed at 800°C for repeat of same measurements; and finally annealed them at 950°C for repeat of same measurements. The final results are not in, but no strong $1.54\text{-}\mu\text{m}$ emission was not observed for the first two anneals.

Er-implanted SiC and GaN

Er was implanted into several pieces of GaN and SiC for PL studies [300 keV at $2.0 \times 10^{14} \text{ cm}^{-2}$]. A piece of Si was also implanted to serve as a SIMS witness to check the implant, which was done with a positive result. Thus the

Er implants were all good at the fluence intended. The SiC was grown by CREE and was supplied by Prof. R.F. Davis. of NCSU. The GaN came from three sources, UCSB (MOCVD, via J.M. Zavada), CMU (MOCVD, by A.Y. Polyakov via R.G. Wilson), and HRL (MBE via RGW). O was not implanted into any of these samples -- because the GaN materials may have enough O in them as grown; O was to be implanted later if it appeared that more O were to be needed; the SiC is already 50% C, an electro-negative ligand, and the Si SIMS witness needed none. The SiC piece was broken into two pieces and there were two pieces each of CMU and HRL GaN implanted. One set of these samples was combined with the piece of Er+O-implanted GaN that was used to obtain the PL data reported in the early Appl. Phys. Lett. identified as Er 81 - and sent to Uwe Hoemmerich at Hampton University for PL measurements. No good PL emission was found in any of these samples, other than in the old Er 81 reference standard. These samples were subsequently implanted with O and returned to Hampton for PL, but again with negative results. The reasons for this lack of success remains unanswered.

Some, if not all, of these materials may require annealing at higher temperatures than the 675°C that has been found to be adequate for Si. SiC and GaN require temperatures greater than 1000°C to activate implanted electrical dopants, so such temperatures may be required to activate implanted optical dopants as well.

Two samples of GaN were sent by Prof. Pearton to Dr. Reiner Vianden in Bonn Germany for "implantation of Er and lattice location," using RBS, with the following significant results, which are quoted from a letter from Vianden. "After implanting both samples with $5 \times 10^{14} \text{ cm}^{-2}$ Er and one additionally with O, and after annealing at 600°C for 30 min, the lattice damage recovered nicely, with minimum yield (RBS χ_{\min}) for the c-axis of about 12 % in the case of the Er+O implanted sample, and only 20 % in the case of the Er-only implanted sample. In both cases, the Er dip overlapped the host dip completely, indicating complete substitutionality of the Er. Further, it is clear that Er occupies the Ga site." Vianden notes that greater fluence of O might help (from reading the literature), as we have been doing in appropriate cases.

SiGe and SiGeC

Collaborative work was carried out with Prof. James Kolodzey and his students at University of Delaware, where they are growing and characterizing SiGe and SiGeC with varying stoichiometry. Our primary role was to

characterize these materials for C and Ge content, for the presence, concentration, and depth distributions of unintentional impurities such as H and O, and intentional dopants such as B or Er. Er is of interest for the emission of the characteristic wavelength of 1.54 μm . This radiation was characterized using PL measurements at HRL and by Prof. Uwe Hoemmerich and his students at Hampton University in VA.

Ion implantation was used to create calibration standards for the SIMS characterization studies (H, C, O, Si, Er) and to dope the various SiGeC materials with Er by implantation. SIMS standards for the determination of the Ge concentration were also prepared using MBE growth of a layered structure SiGe with varying Ge concentrations. The MBE standards were prepared by Edward Croke, III, of HRL.

The results of one study are: Two samples of Er-doped SiGeC were analyzed. The Ge concentration was measured to be 33% and the C, about 0.2%. The Er concentration was measured to be about 0.7% (or $3.5 \times 10^{20} \text{ cm}^{-3}$). A SIMS profile of one Er-doped SiGeC layer is shown in Fig. 13 (Oct 3/4)

SIMS studies of grown-in Er-doped MBE SiGeC

Samples of SiGeC with approx. 30% Ge and 1% C and grown-in Er doping were supplied by Prof. James Kolodzey and his students at University of Delaware. We carried out SIMS measurements to determine the doping density and depth distribution of the grown-in Er. Samples # 160 and #161 were measured for Si, Ge, C, and Er using SIMS. Er is present in a layer about 0.1 μm thick at a concentration of about 0.6 % (density of about $5 \times 10^{20} \text{ cm}^{-2}$). Ge is about 33 % and C is about 0.2 %.

Samples #139, #140, & #141 were implanted with Er at 300 keV and $1.0 \times 10^{14} \text{ cm}^{-2}$. Each sample was then cleaved into three pieces. One piece from each sample was then annealed at each of three temperatures, 600, 650, and 700°C for 10 min. The nine samples were then returned to Univ. Delaware for PL measurements. These samples were not additionally implanted with O. The results of this work were written up at Univ. of Delaware..

Study of ^2H in Ge, SiGe, and SiGeC and comparisons

For bulk Ge (from RGW and from Univ. FL): ^2H was implanted in bulk Ge at 15 keV and $5 \times 10^{15} \text{ cm}^{-2}$, and annealed at temperatures of 150, 200, 250, 300, 350, 400°C. The resulting depth distributions were measured using SIMS, as shown in Fig. 14. A classical case of redistribution of H is seen -- toward the surface from the implant peak, but with a rather abrupt acceleration between 350 and 400°C.

Bulk Ge(p), ^2H plasma-treated: Bulk Ge was also treated with a ^2H plasma at 250°C. The resulting depth profile was almost identical to similar profiles for experiments in Si.

Epitaxial Ge on Si (from Univ. DE): ^2H was implanted into Ge grown epitaxially on Si, at 20 keV and $5 \times 10^{15} \text{ cm}^{-2}$. Pieces were annealed at 300, 350, 400, 450°C. The resulting depth distributions were measured using SIMS; see Fig. 15. For all four annealing temperatures, the Ge moves to the interface with the Si substrate. The peak of the profile moves slightly toward the surface, as if decorating the damage depth distribution. The density of the profiles decreases somewhat, but remains within a factor of 5 of the as-implanted density. There is no evidence that H is moving to the surface as is has in other materials, which is interesting -- the chemical potential of the defects at the interface is apparently stronger than that of the surface.

Ge/Si ^2H plasma-treated A similar sample was treated with a ^2H plasma at 250°C. The Ge layer is $\sim 0.4 \mu\text{m}$ thick. The ^2H redistributes to "fill" the Ge layer, but penetrates into the Si substrate where it is about $3 \times 10^{17} \text{ cm}^{-3}$, apparently to great depth. The ^2H density is high at the surface ($3 \times 10^{20} \text{ cm}^{-3}$) and decreases through the Ge layer to $3 \times 10^{19} \text{ cm}^{-3}$.

Epitaxial SiGe on Si (from Univ. DE): A study of the redistribution of hydrogen in $\text{Ge}_x\text{Si}_{1-x}$ on Si as a function of x value was carried out. Material with different x values was provided by Univ. of Delaware, and implanted identically with ^2H at 15 keV and $5 \times 10^{15} \text{ cm}^{-2}$. These samples were annealed at temperatures of 300, 400, 500, and 600°C, and the resulting depth profiles were measured using SIMS. The results are shown in Figures 16, 17, 18, and 19. The values of x for the four cases are 1,

0.7, 0.6, and 0.35 (or less - by SIMS). The hydrogen diffuses toward the substrate interface, and reaches it for temperatures greater than 500°C. The data are similar for all value of x, but differ in detail.

SiGe/Si ^2H plasma-treated. A sample of GeSi was treated in a ^2H plasma at 150°C. See Fig. 20 for the resulting depth profiles measured using SIMS. The Ge layer is ~0.35 μm thick. The ^2H penetrates less than in the GeSi layer treated at 250°C. The ^2H density is high at the surface ($>10^{21} \text{ cm}^{-3}$) and decreases precipitously to 10^{16} cm^{-3} (5 orders of magnitude) in just more than 0.1 μm . The Ge layer is only about 0.3 μm thick. There is a low density of ^2H region at 0.2 μm that is not understood, deeper than which the ^2H density goes to the same $\sim 3 \times 10^{17} \text{ cm}^{-3}$ value in the Si substrate, as it is in the Si substrate.

III-Nitrides

Research related to the growth, characterization, and fabrication of devices in the III-nitrides, including GaN, AlN, GaAIN, InGaN, and InAlN, has been a significant effort on this contract. III-nitrides are currently of great interest for both optical and electronic devices and applications, including blue, green, and violet LEDs and high power/high temperature electronics (microelectronics, especially microwave, more specifically). Our contributions in this field include ion implantation for doping and co-doping (Mg, Ca, P, C, Si, Er, and other rare elements) and for impurity characterization using SIMS (H, C, O, Si,); SIMS measurements of both intentional and unintentional impurities -- both the concentration and depth profiles of these impurities. See papers 13, 15, 18, 23, and 27 in the list at the end of this report for papers directly related to device processing, and papers 6, 7, 11, 12, 37, 38, 39, and 44 for papers that support device processing.

PL measurements are another important area of work in these nitrides. PL measurements were made both at HRL and at Hampton University (Prof. U. Hoemmerich). Papers in this area resulted and are listed as 9, 30, 31, 33, 42, 43, and 46.

GaN on SiC (2 samples) and GaN on sapphire (2 samples) from Richard Shealy at Cornell Univ., three grown using OMVPE and one using MBE, were studied using SIMS. A special study was made of Cr, Mn, and Cr by high mass

resolution in nitrides that worked very well - a new valuable analysis technique for stainless steel contamination.

GaN on sapphire grown using OMVPE from Marek Skowronski at Carnegie Mellon Univ. - with varying growth temperature, Si doping, etc. was also studied using SIMS. Six layers 0.5 μm thick were grown on GaN or AlGaN, each layer with different conditions, with a cap of GaN when AlN was grown last. C tracks the growth temperature; O does not (much less) -- O was expected to, so O is not a function of growth temperature. NH₃ is the suspected source of O. Si doping tracks the intended growth.

Pr-implanted materials

We implanted Pr at 300 keV and $1.0 \times 10^{14} \text{ cm}^{-2}$ into three pieces of GaN (grown at NCSU, HRL, and UNM) and pieces of SiGe (from U DE), sapphire, Si (witness), and GaAs. The samples of GaN, Si, and GaAs were subsequently implanted with O at 40 keV and $1.0 \times 10^{15} \text{ cm}^{-2}$. The sapphire is assumed to need no additional O, and the SiGe material was scheduled for a set of measurements to begin without O and then to have O added. All samples were then annealed at 675°C for 10 min and sent to Uwe Hoemmerich for PL measurements. However no stimulated emission was observed at 1.3 μm , possibly because of the lower Pr density. In the meanwhile, a SIMS measurement was made on the Si witness for the Pr implant and found to contain too little Pr. Pr was present but at a concentration far below the intended $1 \times 10^{14} \text{ cm}^{-2}$. These samples were subsequently returned to HRL for re-implantation of Pr and anneal. Pr was again implanted, with a Si witness, which showed the correct Pr concentration via a subsequent SIMS measurement made on 16 Dec. These samples were then combined with the Er-implanted samples that had O added and all subjected to an intended 675°C anneal. However the temperature controller failed and the temperature exceeded 900°C but the exact temperature is unknown; it was between 900 and 950°C. While this higher temperature may be harmful for a few sample, it was possibly very good for the samples of SiC, GaN, and sapphire, all of which may require a higher temperature to active the implanted dopants -- as high as greater than 1000°C. See the explanation in the section titled Er-implanted SiC and GaN.

Oxidized AlN and InAlN

As-grown and oxidized samples of AlN and InAlN were studied using SIMS. Some samples were prepared at the University of Delaware in Professor Johnson Olowafe's group and Prof. J. Kolodzey's group. Some of this work has been published; see reference 40. Four samples were analyzed, two as-grown and two oxidized. It appears that where ever O is introduced, the O replaces the N and AlO is formed, not AlN. Si is very high in all samples. H, C, O, are high in the as-grown samples. H and C are lower in the oxidized sample. For reference, measured low values of H, C, O, and Si in III-nitrides are in the 10^{17} and 10^{18} cm^{-3} ranges.

III-nitrides grown by pulsed laser deposition at UCLA

Students at UCLA working under Professors S. Williams and P. Gillis grew III-nitrides using pulsed laser deposition. They grew such films also doped with lanthanide rare earth elements (Pr, Nd, Er, Yb). We characterized these films using SIMS, and attempted to measure the optically stimulated emission of $1.54\text{-}\mu\text{m}$ light from them using PL measurements. SIMS measurements showed that these films do contain the intended rare earth element in concentrations of the order of 1%. SIMS measurements also showed that these films have high concentrations of impurity elements (H, C, O, Si, and others), probably as the result of impure starting materials for the GaN or AlN and for the rare earth elements. For this reason, we examined their starting material using SIMS. The starting GaN powder was pressed into pellets. One of those pellets was used as a target for SIMS analyses using both positive ion mass spectrometry (oxygen primary ion beam) and negative SIMS (cesium primary ion beam). The two most intense elements were Ga and N. However, many impurity elements are present, some with concentrations greater than 1 %. The more abundant elements measured using positive SIMS were: C, O, Al, Ca, Ti, Cr, Fe, Y, Nb, and In; less abundant elements were Li, Na, Mg, K, V, Cu, Mo, and Er. The more abundant elements measured using negative SIMS were: C, O, Se, and molecular C or graphite. Less abundant elements included Cl, Fe, and I. Some of these elements no doubt came from the press material (steel) and from other materials used previously in the press (pressed materials). Detailed semiquantitative analyses could be carried out if it became important enough to provide the funding to do so. SIMS measurements were also carried out on a

sample of GaN made using a LIL process. This sample contained large concentrations of Li and I (more than 50% Li).

Initial PL measurements showed no stimulated emission. Another student grew layers of Er-doped GaN that were analyzed and found to contain Er.

Summary of collaborative work with University of Delaware

We worked with Professor James Kolodzey and his students, and some with Professor Johnson Olowolafe at the University of Delaware during most of the time of this program. Here we list that work by student, time, and material and sample number).

Dimitry Hits: 1995 GeC:B and SiGe superlattices

Bradley Orner: 1995/1996 SiGeC Implanted SiGeC with Er, with Er plus O, and with ^{2}H , plus annealing for PL measurements. Observed $1.54\text{-}\mu\text{m}$ emission by PL, and an intense line at $1.61\text{ }\mu\text{m}$, in all six samples implanted with Er. SIMSed various samples for H, C, O, and Si content and depth profile.

Fen Chen: 1996 GeC:B

Enam Choudhury: 1996/1997 Oxidized AlN and GaN

Mike Dashiell: 1997 GeC:P for P and Ge content, and for B doping density, and for Ga impurity

Prof. Olowolafe: 1996/1997 Oxidized AlN for H, C, O, Si content

Miscellaneous work and supporting efforts at universities and other laboratories

We measured the depth distribution, using SIMS, of ^{2}H in samples D1495 & 1503 from Bertrand Theys of CNRS in France (See Fig. 21)

We implanted Er into LiNbO_3 to create a SIMS standard for Prof. Robert Tavlykaev at Univ. Florida.

We measured, using SIMS, the composition and impurities of XXXX for Prof. Russ Dupuis and student (?) Ram Chalkara from Univ. Texas at Austin.

We measured the depth distributions and densities of H, C, O, and Si in four samples of GaN grown at Carnegie Mellon University (Prof. Marek Skowronski).

Using SIMS, we measured ^2H profiles in 3C SiC - implanted and annealed - for Prof. Andrew Steckl of Univ. Cincinnati.

Using SIMS, we measured depth profiles of Er grown doped in GaN, and also of H, C, O, Si impurity densities and depth distributions for Prof. Andrew Steckl of Univ. Cincinnati.

We measured depth distributions of Mg (grown doped) and impurities H, C, O, and Si, in five samples of GaN grown at Sandia National Laboratory (Jung Han), using SIMS.

We measured depth distributions, using SIMS, of ^2H in AlN plasma treated with ^2H for Univ. Florida.

We carried out a SIMS study of impurities in samples of InN grown using MMBE at Univ. Florida (Prof. Cammy Abernathy).

Collaborative work with Sandia National Laboratory (Dr. John Zolper, who, during this contract time, left Sandia to fill the opening at Office of Naval Research vacated by Max Yoder, who was promoted) (and with Prof. Steve Pearton at Univ. of Florida): We analyzed, using SIMS, samples of GaN implanted with Be, C, Zn, and Cd into samples of GaN and annealed, supplied by Sandia. We implanted samples of GaN supplied by Sandia with ^{18}O and Ca, to be added to this study of annealing and redistribution, using SIMS. This work resulted in several papers, namely 12, 13, 23, 32, and 38, in the list at the end of this report.

Meetings with ARO personnel

R.G. Wilson and R.N. Schwartz of HRL met with J.M. Zavada on several occasions to discuss results obtained on the contract program, to discuss future experiments and direction for the program, and to discuss conference presentations and journal papers. Dates and locations of some of these meetings are listed below:

6-9 Aug 1996	University of California at Santa Barbara, and HRL Malibu
10-12 Sept 1996	Tours France (RGW only)
24-25 Oct 1996	HRL Malibu CA
16 May 1997	HRL Malibu CA
16 Oct 1997	Stevenson Ranch CA (RGW only)
15-17 Mar 1998	C. Evans and Associates, Sunnyvale CA; and ARO Workshop at Asilomar Conference Center, Pacific Grove CA

In conjunction with this program, we attended the ARO-sponsored Workshop on New Concepts on 3-D Optical Devices Using Rare Earths and Other Novel Approaches held in Asilomar CA 15-17 Apr 1998

Publications that resulted from this program

1. R.G. Wilson, C.B. Vartuli, C.R. Abernathy, S.J. Pearton, and J.M. Zavada, "Implantation and redistribution of dopants and isolation species in GaN and related compounds," *Sol. State Electron.* **38**, 1329-33 (1995)
2. J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, V. Krishnamoorthy, B. Bharatan, K.S. Jones, and R.G. Wilson, "Growth of AlN by metalorganic molecular beam epitaxy," *Appl. Phys. Lett.* **67**, 253-55 (1995)
3. S.J. Pearton, C.R. Abernathy, C.B. Vartuli, R.G. Wilson, and J.M. Zavada, "Diffusion of implanted dopants and isolation species in III-V nitrides," *Mat. Res. Soc. Proc.* Vol. **354**, 159-164 (1995)
4. S.J. Pearton, C.R. Abernathy, J.D. MacKenzie, R.G. Wilson, F. Ren, and J.M. Zavada, "Thermal stability of deuterium in InAlN and InAlGaN," *Electron. Lett.* **31**, 327-329 (1995)
5. B.A. Orner, A. Khan, D. Hits, F. Chen, K. Roe, J. Pickett, X.. Shao, R.G. Wilson, P.R. Berger, and J. Kolodzy, "Optical properties of Ge_{1-y}C_y alloys," *J. Electron. Matl.* **25**, 297-300 (1996)
6. S.J. Pearton, R.J. Shul, R.G. Wilson, F. Ren, J.M. Zavada, C.R. Abernathy, C.B. Vartuli, J.W. Lee, J.R. Mileham, and J.D. Mackenzie, "The incorporation of hydrogen into III-V nitrides during processing," *J. Electron. Mat.* **25**, 845-49 (1996)
7. S.J. Pearton, C.R. Abernathy, C.B. Vartuli, J.D. Mackenzie, R.J. Shul, R.G. Wilson, and J.M. Zavada, "Hydrogen incorporation in GaN, AlN, and InN during Cl₂/CH₄/H₂/Ar ECR plasma etching," *Electron. Lett.* **31**, 836-37 (1995)
8. S.J. Pearton, C.R. Abernathy, C.B. Vartuli, J.W. Lee, J.D. MacKenzie, R.G. Wilson, R.J. Shul, F. Ren, and J.M. Zavada, "Unintentional hydrogation of GaN and related alloys during processing," *J. Vac. Sci. Technol. A14*, 831-35 (1996)
9. J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, U. Hoemmerich, X. Wu, R.N. Schwartz, R.G. Wilson, and J.M. Zavada, "Er doping of AlN during growth by metalorganic molecular beam doping," *Appl. Phys. Lett.* **69**, 2083-85 (1996)
10. M. Shin, A.Y. Polyakov, M. Skowronski, D.W. Greve, R.G. Wilson, and J.A. Freitas, "Factors influencing the electrical and optical properties of AlGaN layers on sapphire," *Mat. Res. Soc. Symp. Proc.* **423**, 643-48 (1997)

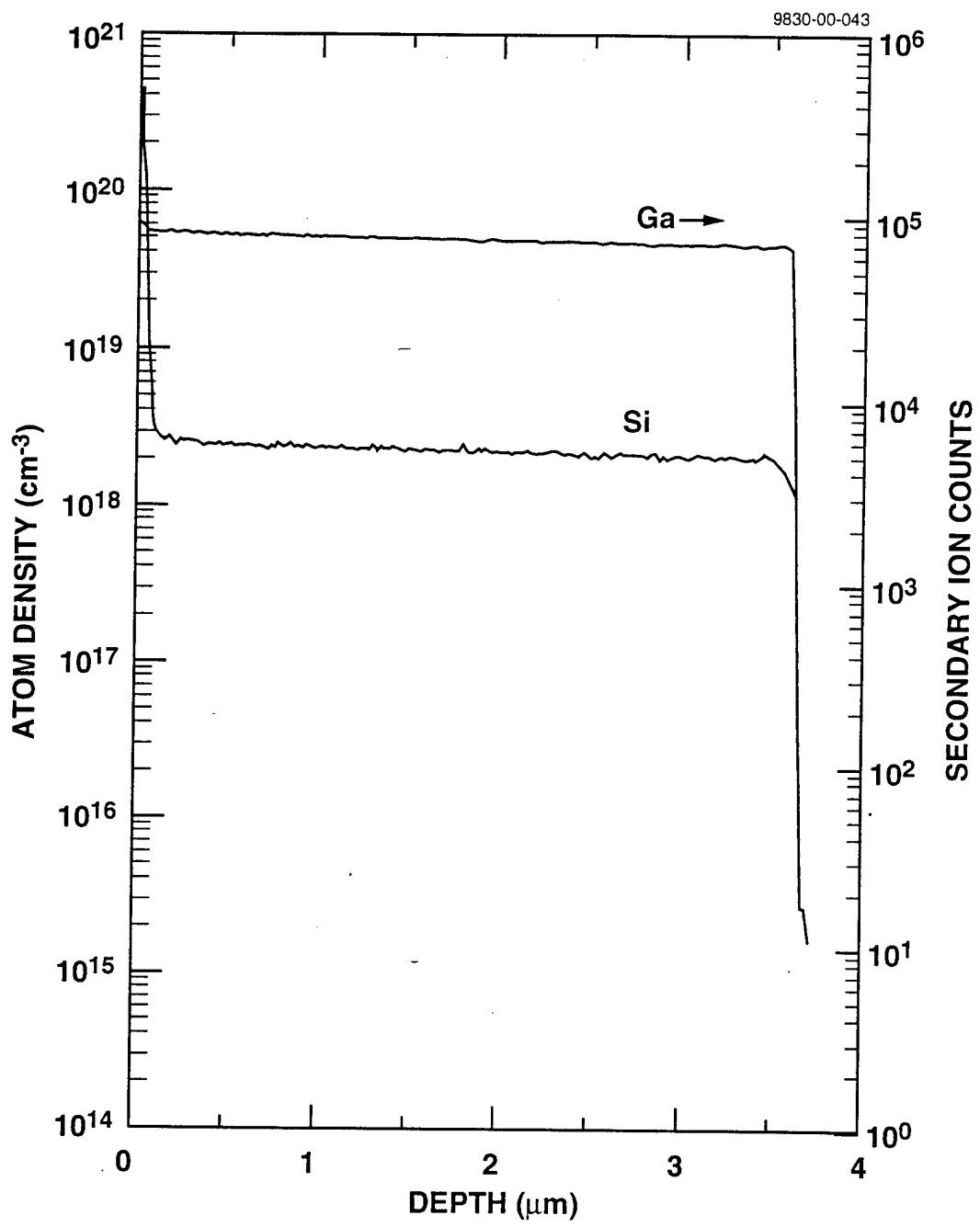
11. C.R. Abernathy, S.J. Pearton, J.D. Mackenzie, J.W. Lee, C.B. Vartuli, R.G. Wilson, R.J. Shul, J. C. Zolper, and J.M. Zavada, "Role of C, O, and H in III-V nitrides," Mat. Res. Soc. Symp. Proc. **395**, 685 (1996)
12. J.C. Zolper, R.G. Wilson, S.J Pearton, and R.A. Stall, "Ca and O implantation doping of GaN," Appl. Phys. Lett. **68**, 1945-47 (1996)
13. J.C. Zolper, R.J. Shul, A.G. Baca, R.G. Wilson, S.J. Pearton, and R.A. Stall, "Ion-implanted GaN junction field effect transistor," Appl. Phys. Lett. **68**, 2273-75 (1996)
14. F. Ren, J.M. Grow, M. Bhaskaran, R.G. Wilson, and S.J. Pearton, "Hydrogen passivation in n- and p-type 6H-SiC," J. Electron. Mater. **26**, 198 (1997)
15. F. Ren, J.R. Lothian, J.D. MacKenzie, C.R. Abernathy, C.B. Vartuli, S.J. Pearton, and R.G. Wilson, "Plasma damage effects in InAlN field effect transistors," Solid State Electron. **39**, 1747-52 (1996)
16. S.J. Pearton, S. Bendi, K.S. Jones, V. Krishnamoorthy, R.G. Wilson, F. Ren, R.F. Karlicek, Jr., and R.A. Stall, "Reactivation of acceptors and trapping of hydrogen in GaN/InGaN double heterostructures," Appl. Phys. Lett. **69**, 1879-81 (1996)
17. R.G. Wilson, "Ion Implantation and secondary ion mass spectrometry of compound semiconductors," Solid State Electron. **39**, 1113-25 (1996) [Review paper]
18. S.J. Pearton, C.R. Abernathy, F. Ren, R.J. Shul, S.P. Kilcoyne, J.D. MacKenzie, M. Hagerott-Crawford, J.C. Zolper, R.G. Wilson, R.N. Schwartz, and J.M. Zavada, "Process development for III-nitrides," Mat. Sci. Engr. **B38**, 138-146 (1996)
19. R.G. Wilson, B.L.H. Chai, S.J. Pearton, C.R. Abernathy, F. Ren, and J.M. Zavada, "Thermal stability of hydrogen in LiAlO₂ and LiGaO₂," Appl. Phys. Lett. **69**, 3848-50 (1996)
20. A.Y. Polyakov, M. Shin, J.A. Freitas, M. Skowronski, D.W. Greve, and R.G. Wilson, "On the origin of electrically active defects in AlGaN alloys grown by organometallic vapor phase epitaxy," J. Appl. Phys. **80**, 6349-54 (1996)
21. A.Y. Polyakov, M. Shin, M. Skowronski, D.W. Greve, R.G. Wilson, A.V. Govorkov, and R.M. Desrosiers, "Growth of GaBN ternary solutions by organometallic vapor phase epitaxy," J. Electron. Mater. **26**(3), 237-42 (1997)

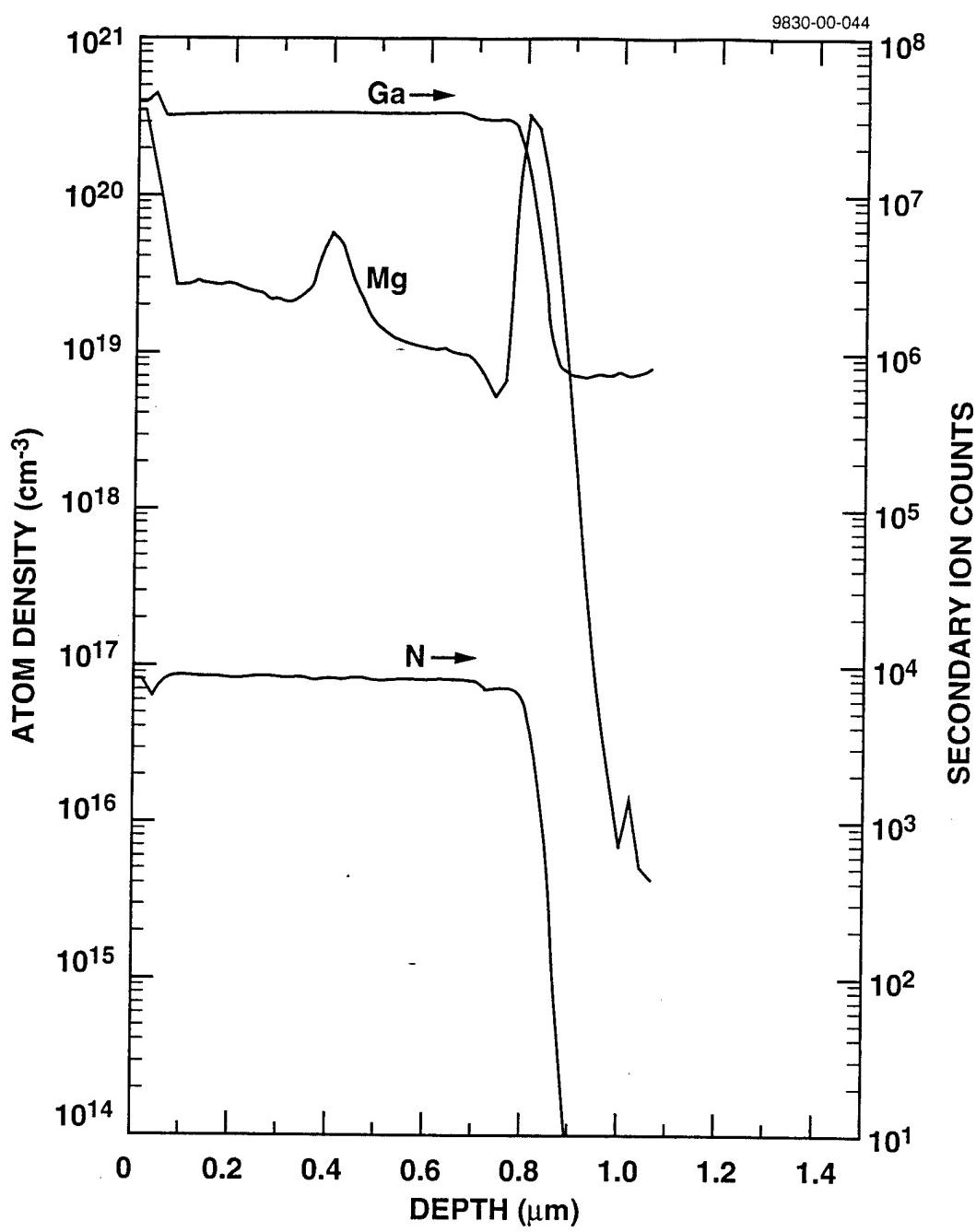
22. A.Y. Polyakov, M. Shin, D.W. Greve, M. Skowronski, and R.G. Wilson, "High resistivity AlGaN layers grown by MOCVD," Proc. European GaN Conf. May 996, Switzerland; MRS Internet Journal Nitride Semiconductor Research 1, article 36 (1996)
23. J.C. Zolper, R.J. Shul, A.G. Baca, S.J. Pearton, C.R. Abernathy, R.G. Wilson, R.A. Stall, and M. Shur, "III-nitride ion implantation and device processing," Electrochem. Soc. Proc. **96-11**, 149-158 (1996)
24. A.Y. Polyakov, M. Shin, R.G. Wilson, M. Skowronski, D.W. Greve, and S.J. Pearton, "Ion implantation of Si, Mg, and C into $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$," Solid-State Electron. **41**, 703-06 (1997)
25. A.Y. Polyakov, M. Shin, W. Qian, M. Skowronski, D.W. Greve, and R.G. Wilson, "Growth of AIBN solutions by OMVPE," J. Appl. Phys. **81**, 1715-19 (1997)
26. G. McDaniel, J.W. Lee, E.S. Lambers, S.J. Pearton, P.H. Holloway, F. Ren, J.M. Grow, M. Bhaskaran, and R.G. Wilson. "Comparison of dry etch chemistries for SiC," AVS Philadelphia, Oct 1996 and J. Vac. Sci. Technol. **A15**, 885-89 (1997)
27. F.Ren, J.R. Lothian, Y.K. Chen, J.D. MacKenzie, S.M. Donovan, C.B. Vartuli, C.R. Abernathy, J.W. Lee, S.J. Pearton, and R.G. Wilson, "Plasma damage effects in InAlN field effect transistors," Mat. Res. Soc. Symp. Proc. **468**, 385-91(1997)
28. C.D. Brandle, F. Ren, R.G. Wilson, J.W. Lee, S.J. Pearton, and J.M. Zavada, "Stability of H in ScAlMgO_4 ," Solid State Electron. **41**, 1943-45 (1997)
29. F. Chen, R.T. Troeger, K. Roe, M.D. Dashiell, R. Zonczyk, D.S. Holmes, R.G. Wilson, and J. Kolodzey, "Electrical properties of SiGeC and GeC alloys," J. Electron. Mat. **26**, 1371-75 (1997)
30. X. Wu, U. Hoemmerich, J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, R.N. Schwartz, R.G. Wilson, and J.M. Zavada, "Direct and indirect excitation of Er^{3+} ions in Er:AlN," Appl. Phys. Lett. **70**, 2126-28 (1997)
31. S.J. Pearton, C.R. Abernathy, J.D. MacKenzie, U. Hoemmerich, X. Wu, R.G. Wilson, R.N. Schwartz, J.M. Zavada, and F. Ren, "Luminescence enhancement in AlN(Er) by hydrogenation," Appl. Phys. Lett. **71**, 1807-09 (1997)
32. J.C. Zolper, S.J. Pearton, R.G. Wilson, and R.A. Stall, "Implant activation and redistribution of dopants in GaN," Ion Implantation Technology - 96, Proc. Eleventh Intern. Conf. Ion Implantation Technology, Austin TX June 1996, 705-08 (1996)

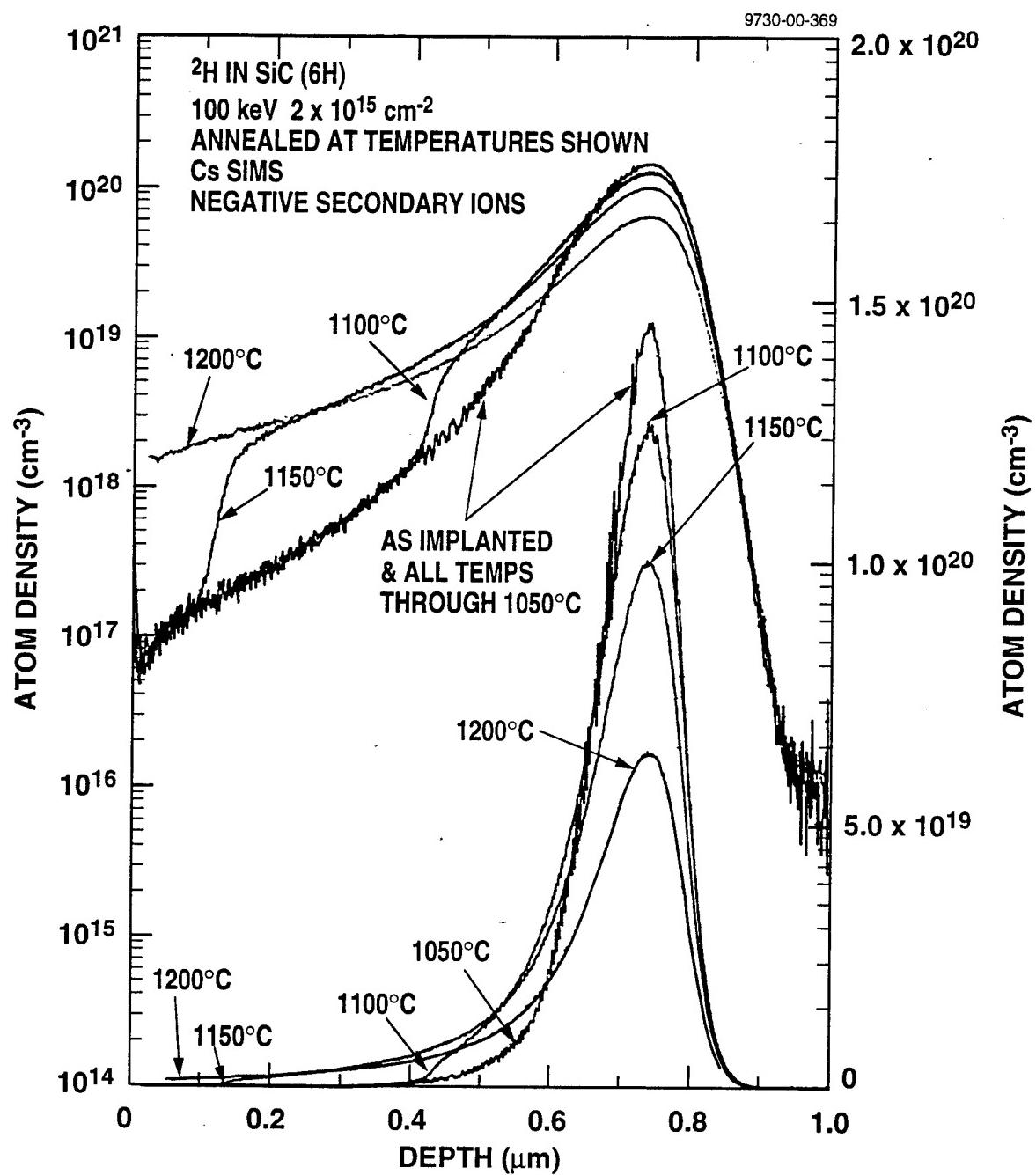
33. X. Wu, U. Hoemmerich, J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, R.G. Wilson, and R.N. Schwartz, "Photoluminescence study of Er-doped AlN," *J. Luminesc.* **72/74**, 284-86 (1997)
34. J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, U. Hoemmerich, X. Wu, R.N. Schwartz, R.G. Wilson, and J.M. Zavada, "Er doping of AlN during growth by metalorganic molecular beam doping," *J. Crystal Growth* **175/176**, 84-88 (1997)
35. S.J. Pearton, C.R. Abernathy, J.D. MacKenzie, U. Hoemmerich, J.M. Zavada, and R.N. Schwartz, "Effect of atomic hydrogen on Er luminescence from AlN," *J. Vac. Sci. Technol. A16*, ~~xxxxx~~ (1998) *in press*
1621-30
36. M. Kumar, J.T. Boyd, H.E. Jackson, J.M. Zavada, H.A. Jenkinson, R.G. Wilson, B. Theys, and J. Chevallier, "Channel optical waveguides formed by deuterium passivation in GaAs and InP," *J. Appl. Phys.* **82**, 3205-13 (1997)
37. S.J. Pearton, J.W. Lee, C.R. Abernathy, R.G. Wilson, J.M. Zavada, and J.C. Zolper, "Electrical and optical properties of C, O, and H in III-nitrides," *Electrochem. Soc. Proc.* **97-34**, 209 (1998)
38. X. A. Cao, C.R. Abernathy, R. K. Singh, S.J. Pearton, M. Fu, V. Sarvepalli, J. A. Sekhar, J.C. Zolper, D.J. Reiger, J. Han, T.J. Drummond, R.J. Shul, and R.G. Wilson, "Ultra-high Si⁺ implant activation efficiency in GaN using novel high temperature rapid thermal process system," 1998 Spring Mat. Res. Soc. Meeting, San Francisco CA, Apr 1998; *Appl. Phys. Lett.* **72**, xxx-xx (1998) *in press*
39. J. Kolodzey, E.A. Chowdhury, G. Qui, J. Olowolafe, C.P. Swann, K.M. Unruh, J. Suehle, R.G. Wilson, and J.M. Zavada, "The effects of oxidation temperature on the capacitance-voltage characteristics of oxidized AlN films on Si," *Appl. Phys. Lett.* **71**, 3802-04 (1997)
40. C.D. Brandle, F. Ren, R.G. Wilson, J.W. Lee, S.J. Pearton, and J.M. Zavada, "Etching and hydrogen incorporation in ScAlMgO₄," *Mat. Res. Soc. Symp. Proc.* **482**, *in press* (1998)
41. S.J. Pearton, R.G. Wilson, J.M. Zavada, C.Y. Song, M.G. Weinstein, and M. Stavola, "Hydrogen in GaN - experiments," *Mat. Res. Soc. Symp. Proc.* **513**, *in press* (1998)
42. U. Hoemmerich, M. Thaik, T. Robinson-Brown, J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, R.G. Wilson, R.M. Schwartz, and J.M. Zavada, "High temperature photoluminescence and photoluminescence excitation spectroscopy of Er-doped GaN," *Mat. Res. Soc. Symp. Proc.* **482**, *in press* (1998)

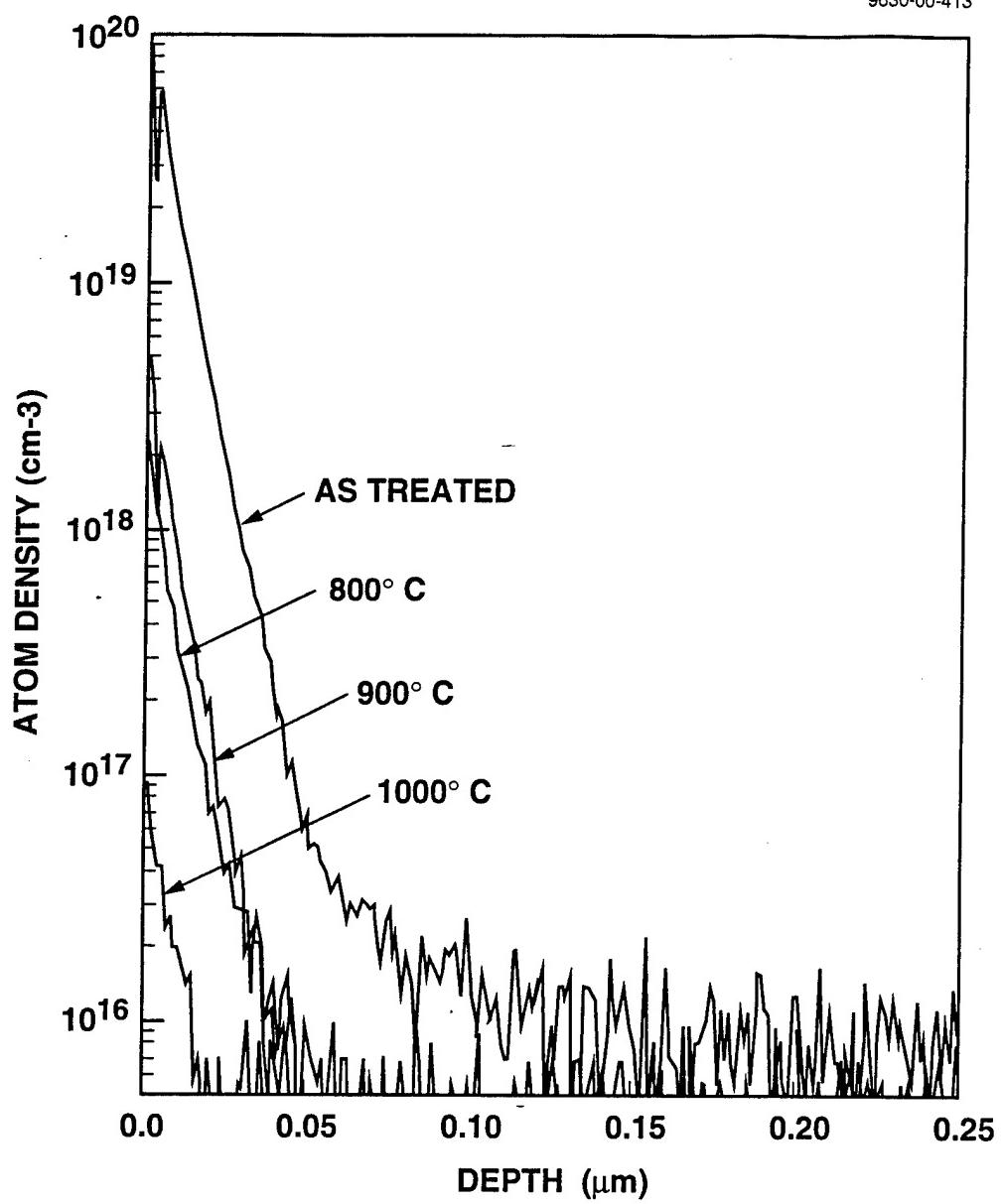
43. M. Thaik, U. Hoemmerich, R.N. Schwartz, R.G. Wilson, and J.M. Zavada.
"Photoluminescence spectroscopy of erbium-implanted gallium nitride,"
Appl. Phys. Lett. **71**, 2641-43 (1997)
44. F. Ren, J.R. Lothian, S.J. Pearton, C.R. Abernathy, C.B. Vartuli, J.D. MacKenzie,
R.G. Wilson, and R. F. Karlicek, "Effect of dry etching on surface properties
of III-nitrides," J. Electronic Mat. **26**, 1287-91 (1997)
45. M.G. Weinstein, C.Y. Song, M. Stavola, S.J. Pearton, R.G. Wilson, R.J. Shul, K.P.
Killeen, and M.J. Ludowise, "Hydrogen-decorated lattice defects in proton-
implanted GaN," Appl. Phys. Lett. **72**, xxx-xx (1998)
46. J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, U. Hoemmerich, J.T. Seo, M.Thaik,
X. Wu, R.G. Wilson, and J.M. Zavada, "Er doping of GaN during growth by
metalorganic molecular beam epitaxy," Appl. Phys, Lett. **72**, ~~xxx-xx~~(1998)

2710-13

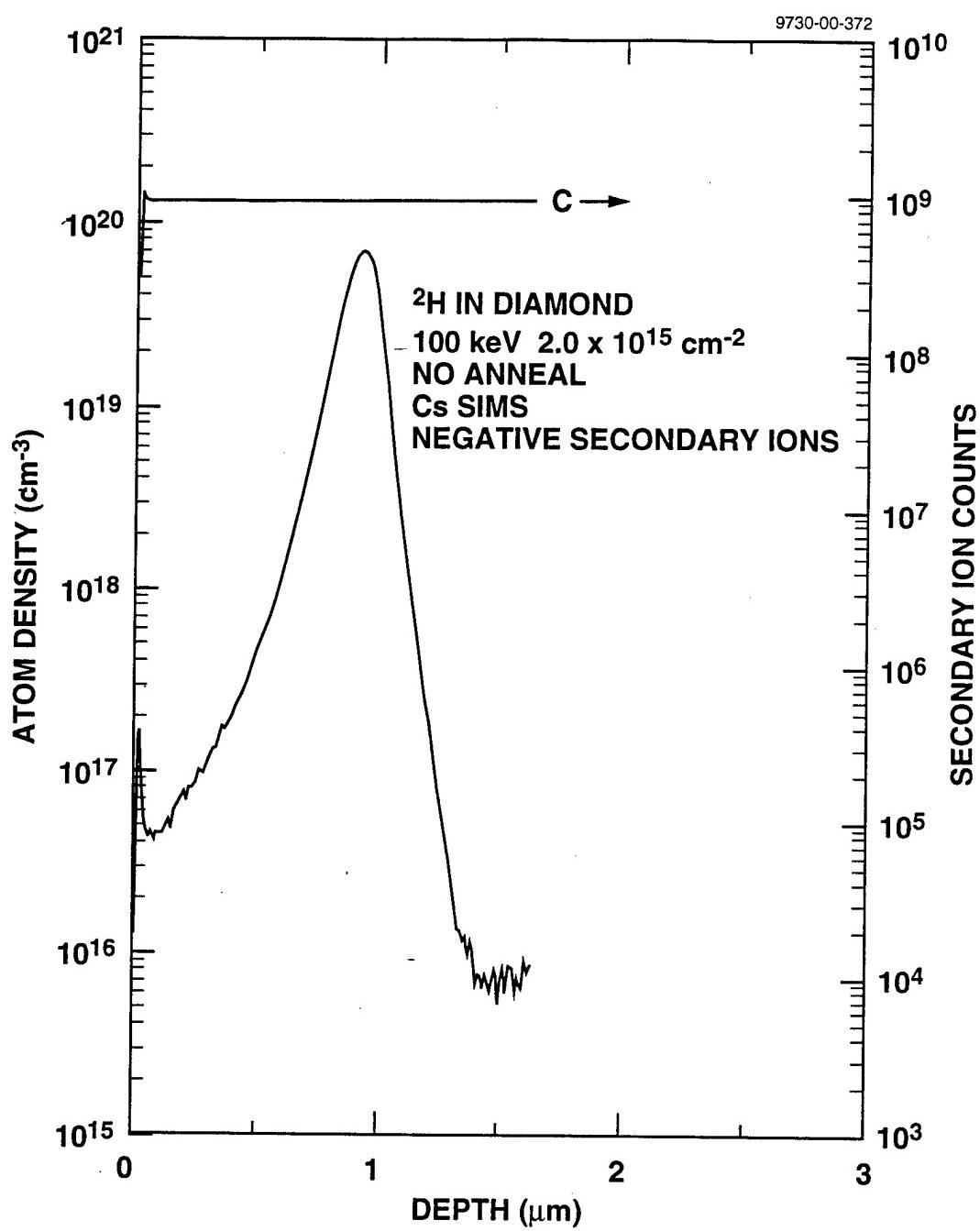


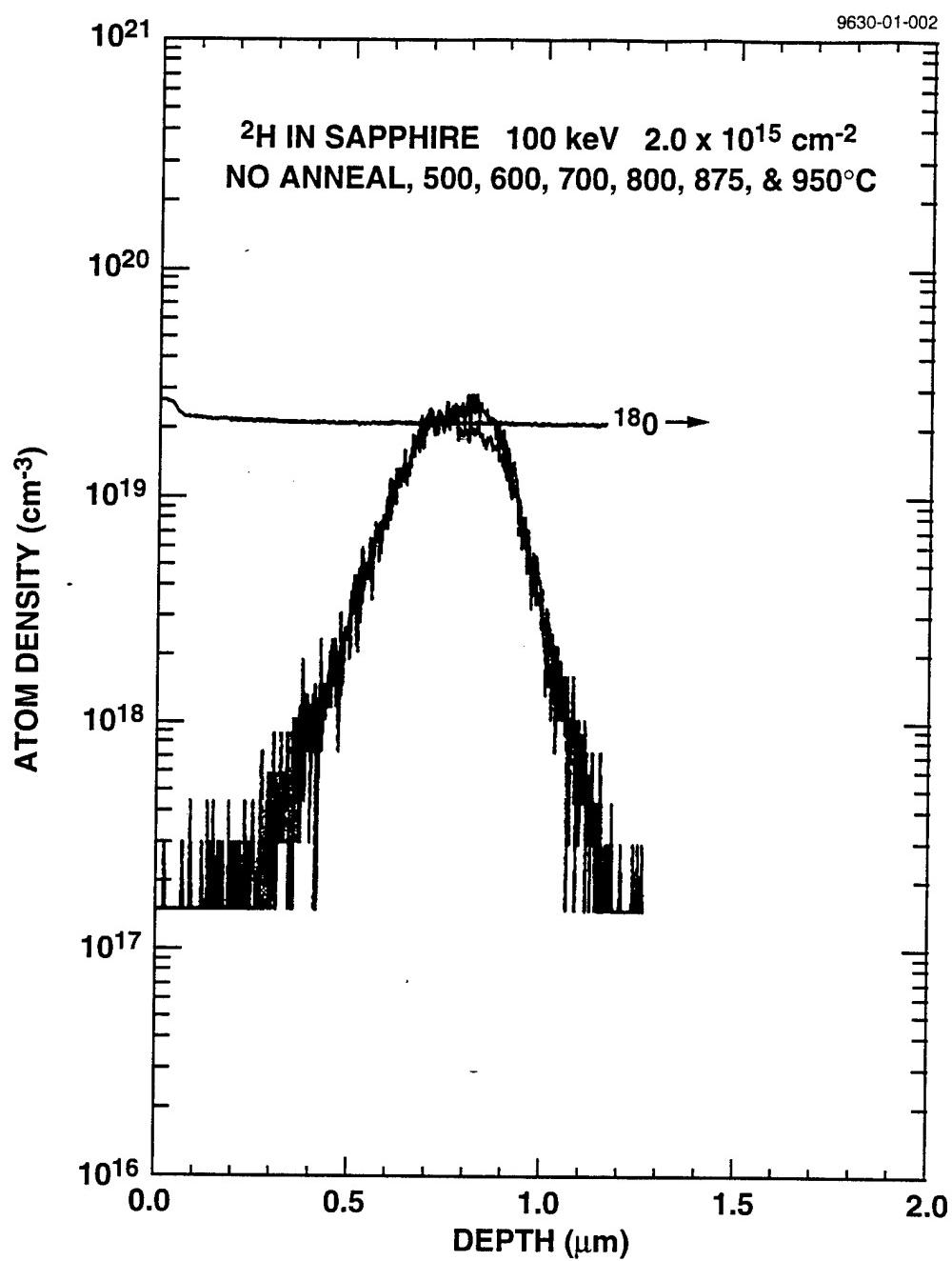


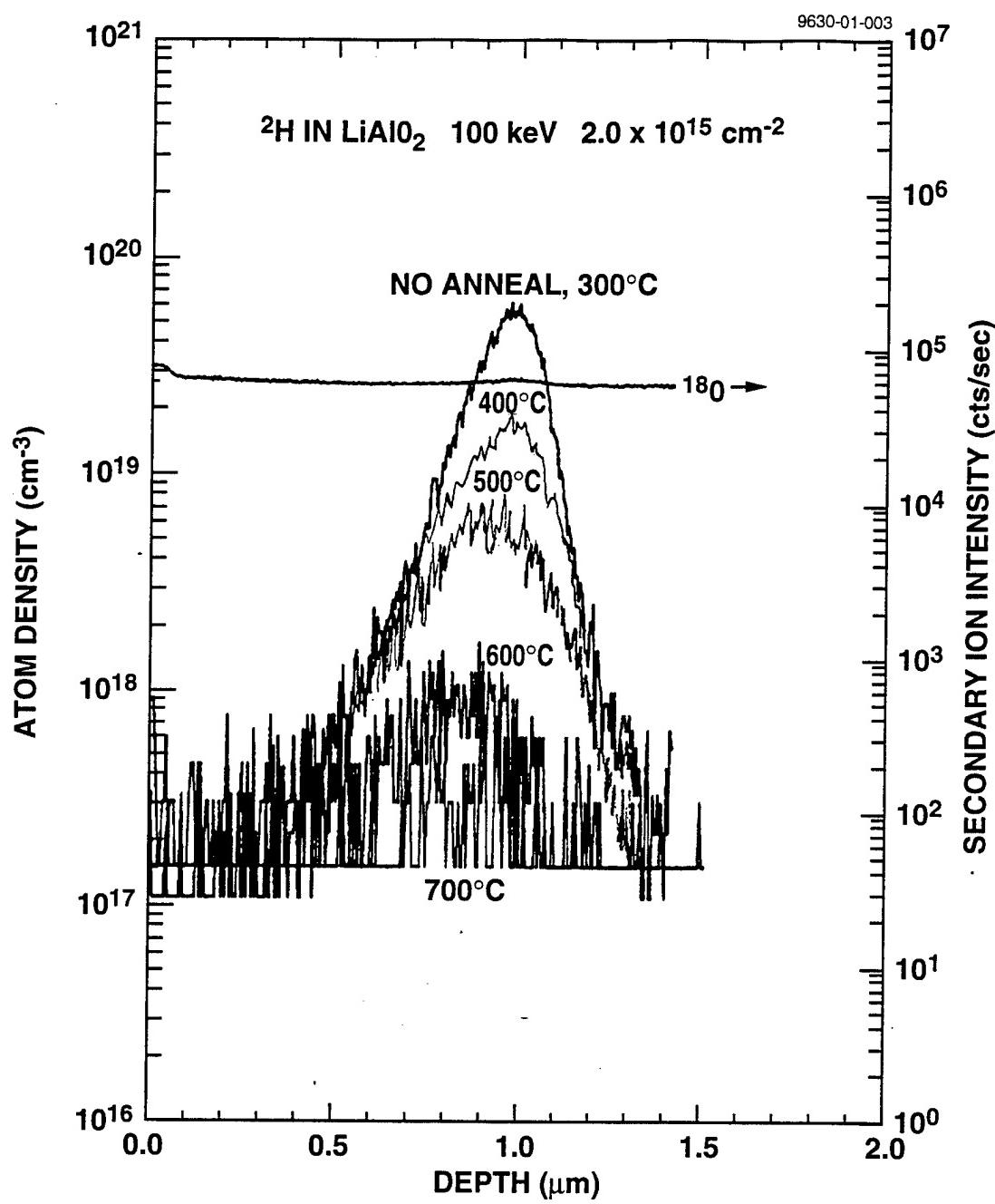


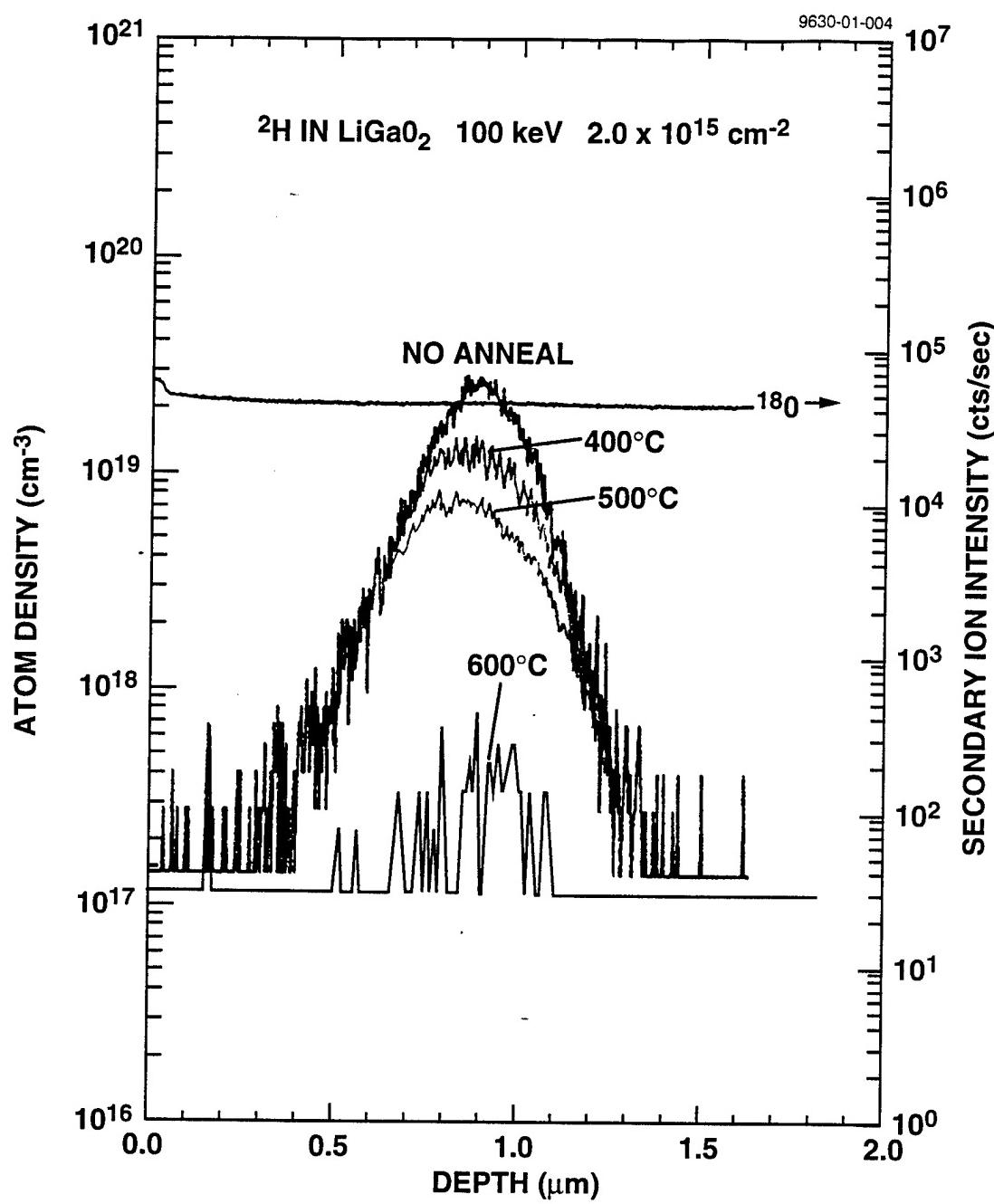


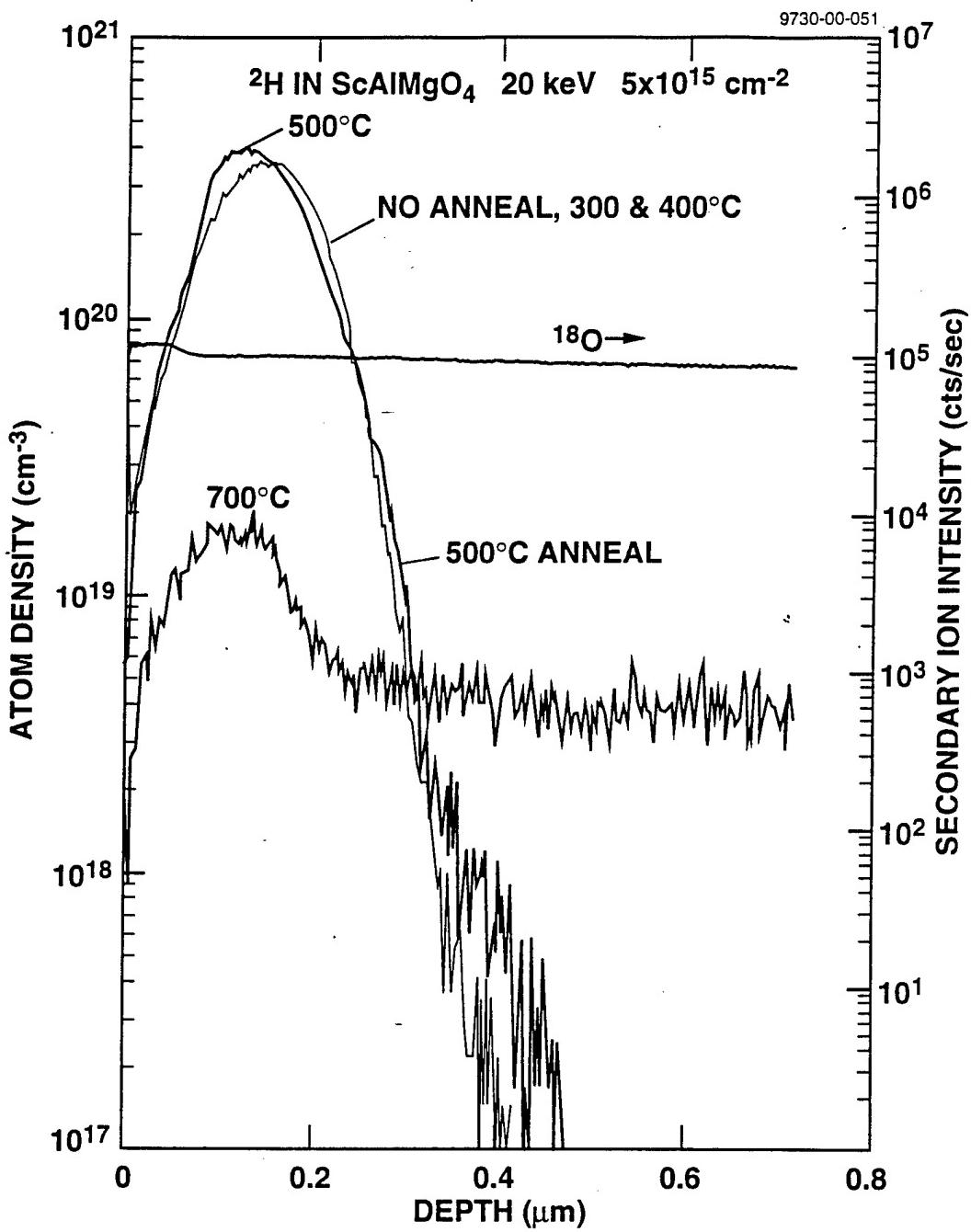
F. 61

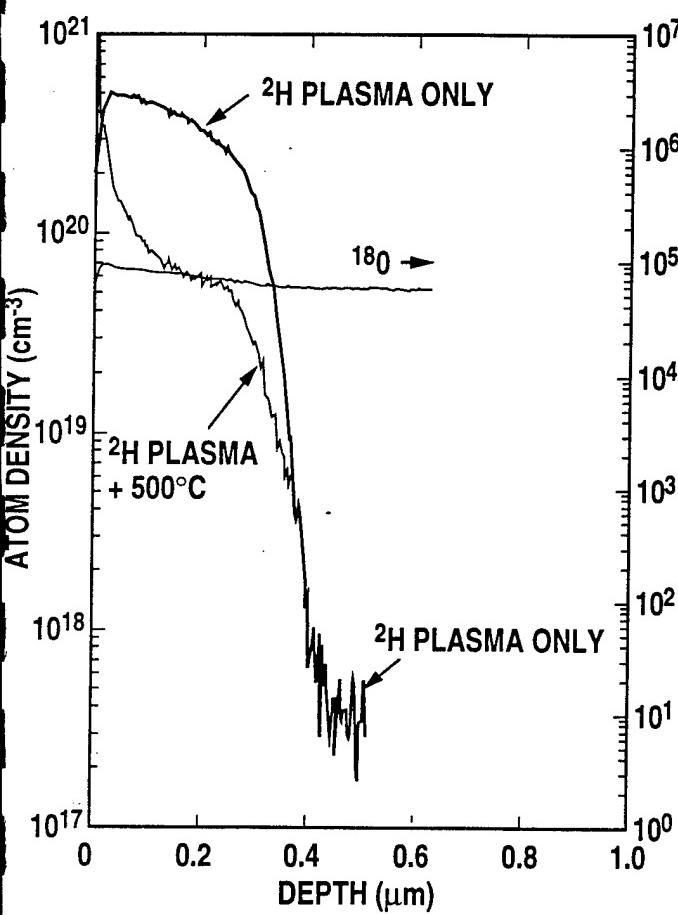




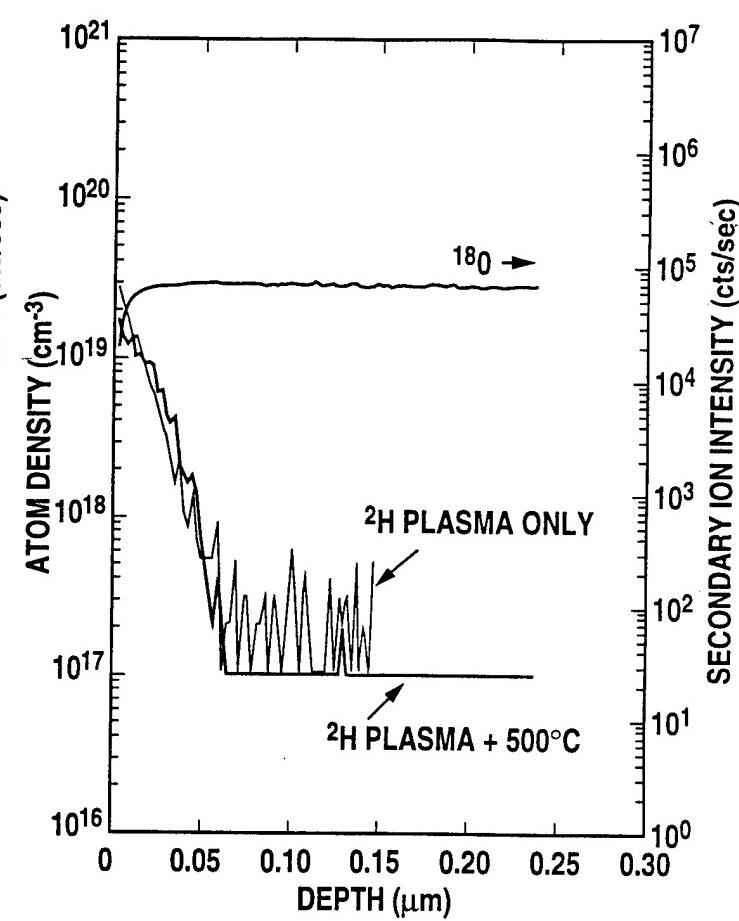








(a)



(b)

